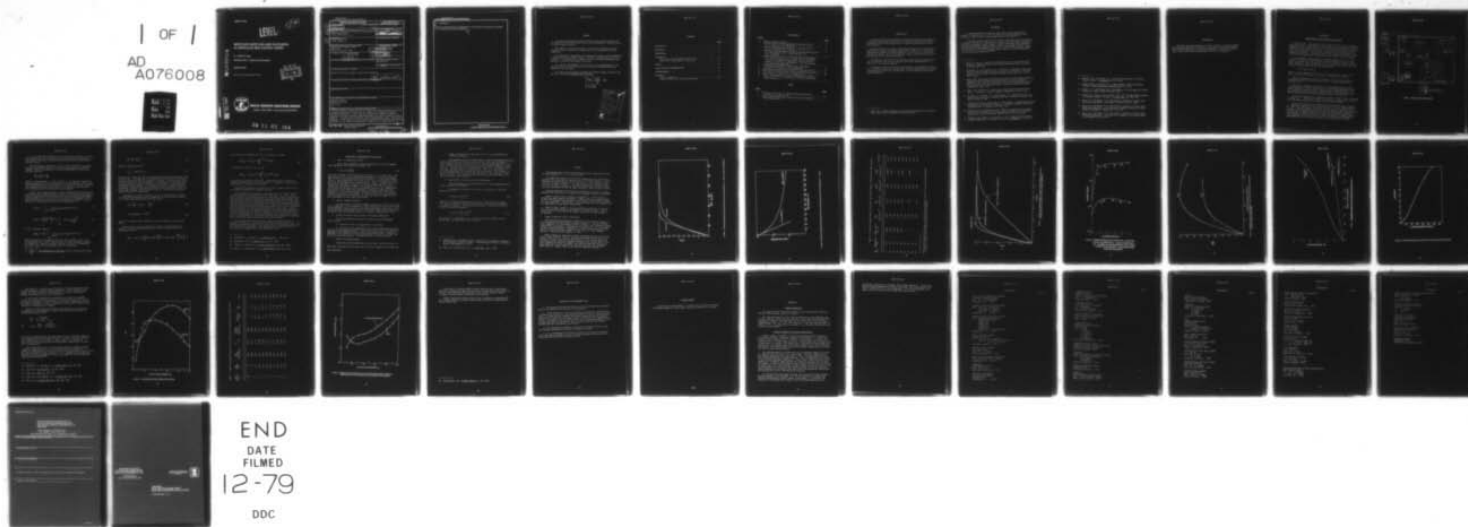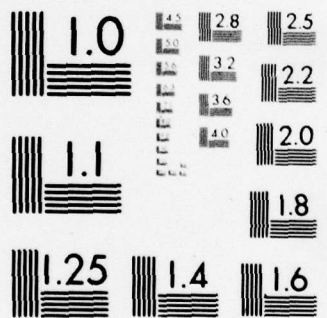AD-A076 008   NAVAL SURFACE WEAPONS CENTER WHITE OAK LAB SILVER SP--ETC F/G 11/9
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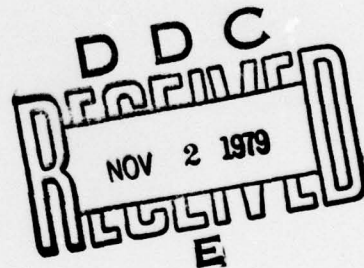
MOISTURE SORPTION AND DIFFUSION IN HERCULES 3501-6 EPOXY RESIN

BY JOSEPH M. AUGL

RESEARCH AND TECHNOLOGY DEPARTMENT

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The objective of this work was to obtain the moisture sorption equilibria of Hercules 3501-6 epoxy resin and its concentration dependent moisture diffusion coefficient. These data are necessary for predicting changes in aircraft structural composites properties where this resin is used as a matrix material. The data were obtained by sorption measurements with a Cahn electrobalance. It was found that the diffusion coefficient is strongly concentration-dependent at low moisture concentration, however, it is fairly flat at

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moisture concentrations corresponding to equilibrium concentration between 30 to 80 percent relative humidity.

SUMMARY

The epoxy resin Hercules 3501-6 will be used as a matrix material for the advanced carbon fiber reinforced structural components to be used in the F-18 Navy fighter aircraft.

The purpose of this work is part of an effort to determine the environmental effects (moisture and temperature) on the properties of these composites.

By combining the experimental and theoretical results of micro-mechanics, a "finite difference laminate theory," diffusion, and modeling of the environment, it is expected that a prediction of the composite performance as a function of time and environment can be made.

The specific investigation of this report is the determination of the moisture sorption equilibrium and the concentration dependent diffusion coefficient of this resin.

This work was sponsored by the Naval Air Systems Command during FY 1978 under the Task Number A3200000/004A/9R02200000.

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INTRODUCTION

This work is part of an effort to characterize pertinent properties of the Hercules 3501-6 epoxy resin which is a material to be used as a matrix in advanced carbon fiber composites for structural application in future naval aircraft.

Moisture affects the elastic and strength properties of organic matrix composites especially at elevated temperatures. This is due to the fact that moisture changes these same properties in the resin. It is therefore desirable to predict the state of moisture sorption with time and the ultimate equilibrium in a given environment.

The specific objective of this work was to determine the moisture diffusion coefficient of the resin and the equilibrium concentration as a function of the relative humidity.

Mechanical properties such as Young's modulus, shear modulus, Poisson's ratio, ultimate strain, and strength have also been determined as a function of temperature and moisture concentration. These results are covered in a separate NSWC/TR.[1]

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1. Augl, J.M. "Moisture Effects on the Mechanical Properties of Hercules 3501-6 Epoxy Resin," NSWC/WOL TR 79-41 (in print).

BACKGROUND

A considerable amount of work has been done to study the effect of moisture on composites. No effort is made to review the subject, suffice it here to refer to some of the original reports and papers.[2-13]

In the two previous reports we have specifically dealt with the questions of moisture diffusion in composites, by using a finite difference approach[14] and with the question of how to model a natural environment where temperature and relative humidity change constantly, and in an irregular fashion. The results of these investigations have led us to believe that property changes of composites in a natural environment under service or storage conditions can be realistically predicted.[15,16]

2. Hertz, J., et al. "Advanced Composite Application for Spacecraft and Missiles," AFML-TR-71-186 Vol II, General Dynamics-Convair, San Diego, California, Mar 1972.

3. Browning, C.E., and Whitney, J.E. "The Effect of Moisture on the Properties of High Performance Structural Resins and Composites," American Chem. Soc., Div. of Org. Coatings and Plastic Chem., 33, No. 2, 1973, pp. 137-148.

4. Augl, J.M., "Environmental Degradation Studies on Carbon Fiber Reinforced Epoxies," Paper presented at the TTCP-Panel P3 Meeting, Melbourne, Australia, 1975, and paper presented at the Air Force Workshop on Durability Characteristics of Resin Matrix Composites, Battelle-Columbus Laboratories, Ohio, 1975.

5. Augl, J.M., "The Effect of Moisture on Carbon Fiber Reinforced Composites. II Mechanical Property Changes," NSWC/WOL TR 76-149, 1977.

6. Browning, C.E., Husman, G.E., and Whitney, J.M., "Moisture Effects in Epoxy Matrix Composites," Composite Materials: Testing and Design, ASTM STP 617, 1976, p. 481.

7. Hofer, K.E., Rao, N., and Larson, D., "Development of Engineering Data on the Mechanical and Physical Properties of Advanced Composite Materials," AFML-TR-72-205, IIT Research Institute, 1974.

8. Browning, C.E., and Hartness, J.T., "Effect of Moisture on the Properties of High Performance Structural Resins and Composites," Composite Materials: Testing and Design, ASTM STP 546, 1974 pp. 284-302.

9. Kaelble, D.H., Dynes, P.J., and Crane, L.W., "Interfacial Mechanisms of Moisture Degradation in Graphite Fibers," J. of Adhesion, 7, 25, 1977.

10. Kaelble, D.H., and Dynes, P.J., "Surface Energy Analysis of Treated Graphite Fibers," J. Adhesion, 6, 239, 1974.

11. Ashbee, K.H.G., and Wyatt, R.C. "Water Damage in Glass Fiber/Resin Composites," Proc. Royal Soc., Series A 312, 553, 1969.

12. Halpin, J.C., and Pagano, N.J., "Consequences of Environmentally Induced Dilation in Solids," AFML-TR-68-395, 1969.

13. Pipes, B.R., Vinson, J.R., and Chou, T.W., "On the Hygrothermal Response of Laminated Composite Systems," J. Comp. Mat., 10, 126, 1976.

14. Augl, J.M., and Berger, A.E., "The Effect of Moisture on Carbon Fiber Reinforced Composites. I Diffusion," NSWC/WOL TR 76-7, 1976.

15. Augl, J.M., and Berger, A.E., "The Effect of Moisture on Carbon Fiber Reinforced Composites. III Prediction of Moisture Sorption in a Real Outdoor Environment," NSWC/WOL TR 77-13, 1977.

16. Augl, J.M., and Berger, A.E., "The Effect of Moisture on Carbon Fiber Reinforced Composites. IV Prediction of Changes in the Elastic Behavior," NSWC/WOL TR 77-61, 1977.

EXPERIMENTAL

The cured resin was machined into plate samples of .024 cm thickness. The diffusion coefficient and moisture sorption equilibria were measured with a Cahn microbalance by sorption measurements. The details of the resin cure and the sorption measurements are given in Appendix A.

DISCUSSION

Measurement of the Diffusion Coefficient

The most direct measurement of the diffusion coefficient of a polymeric material would be to determine the steady state flow of the diffusant through a membrane of the polymer where the concentrations on both sides of the membrane are different but held constant. The diffusion coefficient is then given as the quotient of the flow rate through a unit area divided by the concentration gradient. For dense, pinhole-free films, this method is quite useful and gas chromatographic methods have been devised for this purpose.

For composites, this method has only limited value since it is quite difficult to prepare a thin crack-free composite membrane, though it may serve as a useful check for porosity, which is frequently severe in filament wound composites. Flow through pores is governed by Poisseuille's law, i.e., capillary flow described by the following relation:

$$Q = \pi \, a^4 (p_1 - p_2)/(4 \mu \ell)$$

where Q = volume passing a circular cross section of radius a per second, $p_1 - p_2$ = pressure difference, μ = viscosity coefficient, ℓ = length.

Thus, by changing the pressure difference, it is easily possible to distinguish between diffusion through the solid polymeric material and capillary flow.

Other quite frequently used methods of determining diffusion coefficients of gases or volatile liquids are by sorption measurements where the sorbed vapors are measured either volumetrically or gravimetrically. For the experiments described in this report we have used an electronic microbalance fabricated by the Ventron Instruments Corp., Cahn Division.

The sorption apparatus is schematically shown in Figure 1 and is described in Appendix A. The moisture uptake or desorption is automatically recorded while the vapor pressure and the temperature are held constant.

In an earlier report[13], we determined diffusion coefficients of resins and composites from the initial slope of M_t/M_∞ vs $t^{1/2}$ (M_t = amount absorbed at time t, M_∞ = equilibrium concentration at the respective partial vapor pressure.) The experiments were carried out by exposing rather thick specimens ($5 \times 5 \times 0.3$ cm^3) to some constant relative humidity and constant temperature and weighing the samples from time to time. This method is simple, however time consuming, and therefore not very useful if absorption and desorption measurements are to be carried out until final equilibrium is reached.
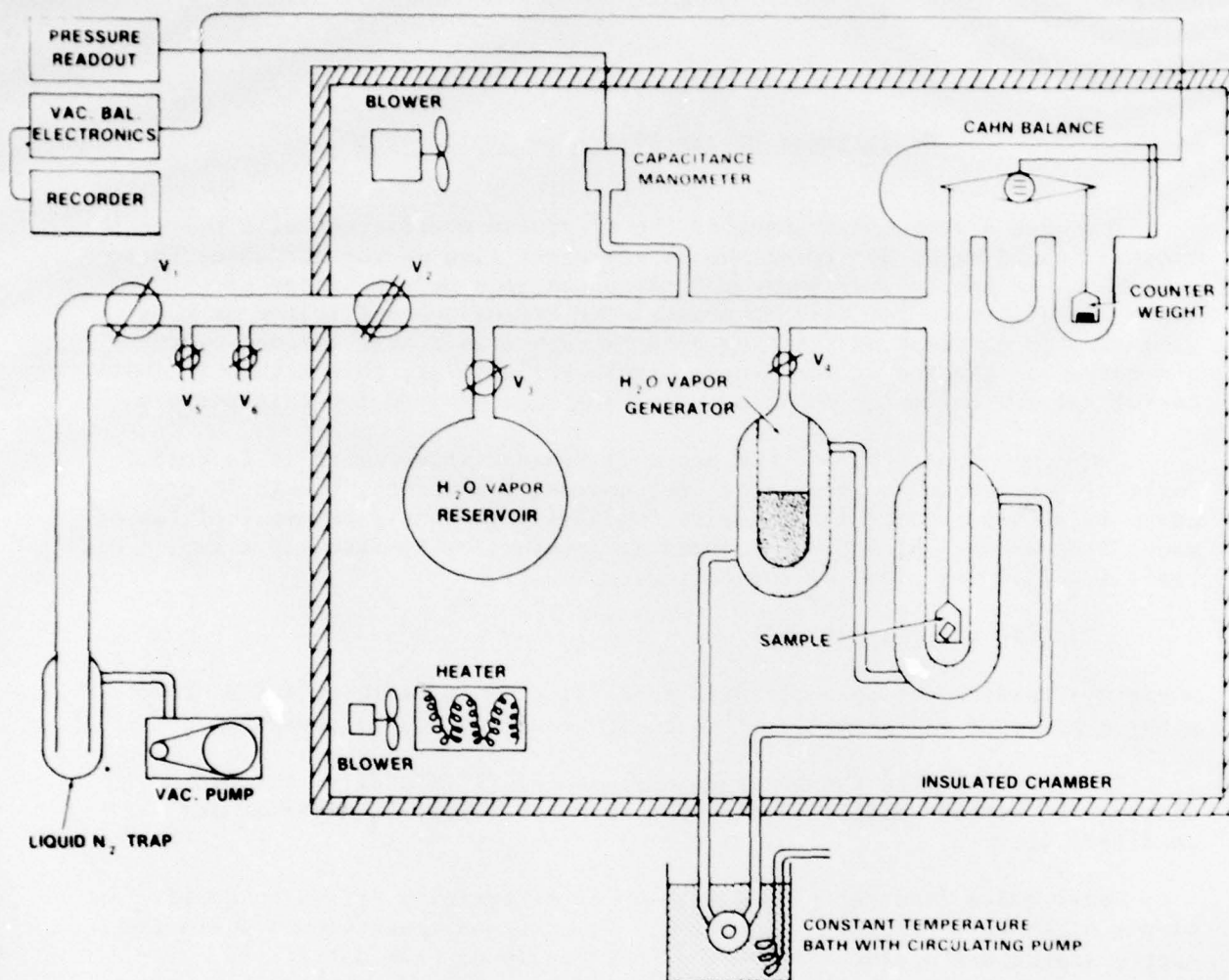
FIGURE 1   MOISTURE SORPTION BALANCE

In our present investigation we were interested in whether or not the 3501-6 epoxy resin had a concentration dependent diffusion coefficient. It was therefore desirable to obtain the total rather than just the initial sorption curves.

The concentration dependence of the diffusion coefficient is usually obtained by performing sorption or permeation measurements at different boundary conditions on geometrically well-defined samples for which the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}[D(c) \frac{\partial c}{\partial x}]$$

(where c = concentration, t = time, and D(c) is the diffusion coefficient which may depend on the local concentration of the diffusant) can be solved. Closed form solutions for Fick's equation are available only for concentration indpendent diffusion coefficients. If D depends on concentration, Fick's equation has to be solved by numerical methods.

Since it may become important to compare experimental data among various laboratories, it might be helpful here to discuss briefly the essential aspects of determining the diffusion coefficient from sorption measurements on plate samples. For a sheet of infinite extension and exposure to the same vapor pressure on both sides, the following closed solution has been derived for a diffusion with concentration independent D.[17]

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp[-D(2n+1)^2 \pi^2 t/4\ell^2] \tag{1}$$

$$M_t/M_\infty = 2 \left(\frac{D_t}{\ell^2}\right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \; \text{ierfc} \frac{n\ell}{\sqrt{Dt}} \right\} \tag{2}$$

and for "longtime" exposure

$$M_t/M_\infty = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-D(2n+1)^2 \pi^2 t/\ell^2] \tag{3}$$

where M_t and M_∞ are the amount of moisture taken up after a time t and at equilibrium (i.e., after infinite time), ℓ = sheet thickness. Formula (2) can be used to derive the useful formulas (4 and 5) for determining D_i^A or D_i^D or $D_{1/2}$ since the summation term in (2) vanishes

17. Crank, T., The Mathematics of Diffusion, 2nd ed., Oxford Univ. Press, 1975.

$$D_i^A = D_i^D = \frac{\pi}{16} R^2 \qquad (4)$$

where $R = d(M_t/M_\infty)/d(t/\ell^2)^{1/2}$

$$D_{1/2} = .049/(t/\ell^2)_{1/2} \qquad (5)$$

the subscript i indicates that D was obtained from the initial portion of the sorption curve. The subscript 1/2 indicates the time after 1/2 of the equilibrium concentration has been absorbed or desorbed. In other words, if the diffusion coefficient does not depend on concentration the results obtained from absorption or desorption experiments are the same. If the diffusion coefficient depends, however, on concentration then D, obtained from such a measurement, is really some average diffusion coefficient which we have, in view of the following, indicated with a bar ($\bar{D}$). Also, then the equality between $\bar{D}^A$ and $\bar{D}^D$ no longer holds.

From equation (3) another formula (6) can be derived which is useful for "longtime" experiments, when the summation can be effectively replaced by its first term from which (6) and (6a) follow:

$$\ln(1- \frac{M_t}{M_\infty}) = \ln \frac{8}{\pi^2} - \frac{\bar{D}\pi^2 t}{\ell^2} \qquad (6)$$

$$[d \ln(M_\infty - M_t)]dt = \pi^2 \bar{D}/\ell^2 \qquad (6a)$$

From this it follows that a logarithmic plot of $(1-M_t/M_\infty)$ vs time becomes linear.

In some cases it may be impractical to wait for equilibrium to be attained. For such cases another useful formula (7) may be derived in a similar way from (3).

$$(M_t)_2 - (M_t)_1 = \frac{8}{\pi^2} \left\{ (M_t)_2 \exp\left[-\frac{\bar{D}\pi^2 t_1}{\ell^2}\right] - (M_t)_1 \exp\left[-\frac{\bar{D}\pi^2 t_2}{\ell^2}\right] \right\} \qquad (7)$$

The concentration dependent $D(c)$ can be obtained by solving

$$\bar{D}_1^A (C_o) = \left(\frac{5}{3}\right) C_o^{-5/3} \int_0^{C_o} c^{2/3} D(C)dC \tag{8}$$

as described by Crank[17] or by solving

$$\bar{D}^D(C_o) = 1.85(C_o)^{-1.85} \int_0^{C_o} (C_o - c)^{0.85} D(C)dC \tag{9}$$

as described by Kishimoto and Enda[18]. Both methods require a series of absorption and desorption curves respectively. Graphical or numerical differentiation is carried out to give $D(c)$.

Frensdorff[19] approached the solution of Fick's equation (where $D(c)$ is concentration dependent) by a numerical method.

He has shown that the slopes of the linear portion of curves of equation (6a) where D is replaced by $D(c)$ are identical, i.e., $-\pi^2/4$. Some authors have called the average diffusion coefficient obtained from the short time solution as "integral diffusion coefficient" while that obtained from the long term solution as "differential diffusion coefficient." These names indicate that the short term solutions were obtained in a process where the diffusion coefficient has a wide range due to the steep concentration gradient while the long term solution requires a measurement close to the equilibrium where the gradient is very flat and therefore the range of $D(c)$ is small. We have therefore used the Frensdorff method for our measurement which makes a numerical integration according to equations (8) or (9) unnecessary and $D(c)$ is obtained directly. $D(o)$, the diffusion coefficient as zero concentration is approached, is also obtained directly from a desorption experiment rather than by an iterative method as described by Crank[20].

Duda and Vrentas[21] have described a complicated method (method of moments) to obtain the total range of $D(c)$ from a single sorption curve. The authors have indicated, however, that highly accurate longtime sorption curves are essential for this method. The authors did not compare the results of their theoretical model with actual experimental data.

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18. Kishimoto, A., and Enda, Y., J. Polym. Sci A, 1, 1799, 1963.

19. Frensdorff, H.K., J. Polym. Sci. A, 2, 341, 1964.

20. Crank, T., and Park, G.S., Trans. Faraday Soc., 45, 240, 1949.

21. Duda, T.L., and Vrentas, T.S., AICHE Journal, Mar 1971, p. 464.

Errors Due to Experimental Inaccuracies

1. Effect of Temperature Control

Over a small temperature range the diffusion coefficient changes with temperature as indicated by equation (10)

$$D = D_o \exp\left(-\frac{E}{RT}\right) \tag{10}$$

as a rule of thumb, D increases by about a factor of 2 for every 10°C. This means that an error in the temperature measurement of 1°C gives an approximate 6% error in the measured diffusion coefficient. If an average temperature of a small temperature fluctuation (+1°C) can be ascertained, the error should be considerably smaller (less than 1%). There is a small error introduced if the experiment is carried out on plate samples that have to be removed from the exposure chamber to be weighted. The error is largest at the initial time periods but gets successively smaller at the longtime exposure because of the square root dependence of moisture uptake with time. Therefore, a continuous measurement of moisture uptake in a closed system by means of a quartz spring balance or a Cahn electro balance is more desirable if accurate data are required. On the other hand, the sample size for such instruments is quite small (100-300 mg).

2. Effect of Sample Thickness

The thicknesses of the sheet samples range usually from .250 to .025 cm for composites. If a micrometer of +.001 cm accuracy is used for the thickness measurement, then the errors in thickness measurements range from .4 to 4 percent and the corresponding diffusion coefficients range in error from .16 to 16 percent since the thickness enters as a square in equations (4) to (7).

3. Effect of Relative Vapor Pressure and Weight Measurements

The error caused by inaccuracies in vapor pressure measurement can be twofold:

a. The error in D(c) is proportional to its slope,

b. The error is also dependent on the accuracy with which the pressure can be held constant during the final phase of the sorption or desorption experiment for determining the slope that enters equation (6a). Similarly important is the accuracy of the weight measurement which must be better than 1% for the long term solution. The combined error in D may reach +12%.

4. Effect of Time Measurement

Since most sorption experiments require times from several hours to many days, time should be the least source of error (assuming the recorder has been calibrated).

5. Range of Usefulness of Equations (4) to (7) for Determining the Diffusion Coefficient

The equations (4) to (7) apply strictly only for determining diffusion coefficients that do not depend on concentration. Even then the range is limited because only one or two terms of the infinite series equation 1-3 were used. Formula (4) gives less than 1% error in the range where M_t/M_∞ is less than 0.5. The same accuracy is obtained with formula (5). Equation (6) gives less than 1 percent error in the range $M_t/M_\infty > 0.7$. In using formula (7), the error depends on both M_1 and M_2 and on the difference. For instance, if M_1 is such that $M_t/M_\infty = 0.5$ and M_2 such that $M_t/M_\infty = .97$, the error is less than 1.6 percent. If M_1 and M_2 are both chosen to be such that $M_t/M_\infty > 0.8$ the error is less than 1 percent.

6. Edge Effects of Plates with Finite Dimensions

A thorough analysis of the edge effects for various geometries was given by Rothwell and Marshall[22].

The correction formula for the short time solution of isotropic materials is [22,23]

$$D = D_o \left[1 + \frac{\ell}{a} + \frac{\ell}{b} \right]^{-2} \tag{10}$$

(where D = corrected diffusion coefficient, D_o = diffusivity for a plate with infinite dimensions (obtained from equation (4)), ℓ = plate thickness, a = length, b = width). For the long term solution (equation (6) and (7)) Rothwell and Marshall suggested

$$D = D_o \left[1 + 2 \left(\frac{\ell^2}{a^2} + \frac{\ell^2}{b^2} \right) \right]^{-1} \tag{11}$$

for a and b $\gg$ 1, and $M_t/M_\infty > 0.6$. These equations were applied for the $\bar{D}_i^A$, $\bar{D}_i^D$, $D_f^A(c)$ and $D_f^D(o)$ given in this report.

22. Rothwell, W.S., and Marshall, H.P., "Analysis of Experimental Transport Data Diffusion of Water in EPDM," Lockheed Missile & Space Co. Technical Report, LMSC-D566642, Oct 1977.

23. Shen, C.H., and Springer. G.S., J. Comp. Mat., 10, 2, 1976.

RESULTS

The specimen used for the sorption and desorption experiments had the following dimensions: 2.5 x 1.8 x 0.024 cm^3.

The sample was exposed in the sorption apparatus at the desired temperature and pressure and the moisture gain or loss was recorded. A typical absorption (A) and desorption (D) curve given by a short term plot (equation (4)) is shown in Figure 2. The same data plotted according to equation (6a) are shown in Figure 3. From the straight line portions of these plots were determined the $\bar{D}_i^A$, $\bar{D}_i^D$, $D_f^A(c)$ and $D_f^D(o)$, values, listed in Table 1.

From the difference in the sorption and desorption curves it is quite apparent that there must be a concentration dependent diffusion coefficient.

Figure 4 shows a plot of M_t/M_∞ vs. $(D_o t/h^2)^{1/2}$. If the diffusion coefficients were constant and equal to 2.08E-10 cm^2/sec as found for $D_f^D(o)$ at 50°C, the absorption and desorption curve should be identical and follow the curve indicated: (theoretical). Using the same scale, one observes that the experimental curves differ considerably.

Figure 5 shows a graph of the resin diffusion coefficient at 30° and 50°C as a function of moisture concentration in weight percent. (From a resin density of 1.274 this can be readily converted in volume percent if so desired.)

Figure 6 shows the ratio of D(c)/D(o).

The equilibrium concentration of moisture in the resin with respect to the surrounding relative humidity is shown in Figure 7. For an AS-carbon fiber composite of a fiber volume fraction of 0.62 the calculated equilibrium concentration of moisture is indicated by the broken line. An actual sample exposed at 80% RH absorbed 1.1539 percent of water which agrees quite well with the calculated moisture uptake of 1.187 (for V_f = 0.62, composite density = 1.5825, and resin density = 1.274).

Figure 8 shows the same data in terms of moisture activity in the resin versus volume fraction. Since at chemical equilibrium the activity a_1 of moisture is equal to the ratio of p/p_o (where p is the partial vapor pressure and p_o is the saturation pressure of moisture over liquid water at the given temperature) there is a simple relationship of moisture activity at equilibrium and relative humidity at which the experiment was performed: %RH = 100 x a_1. (Such a plot is also called a sorption isotherm.)
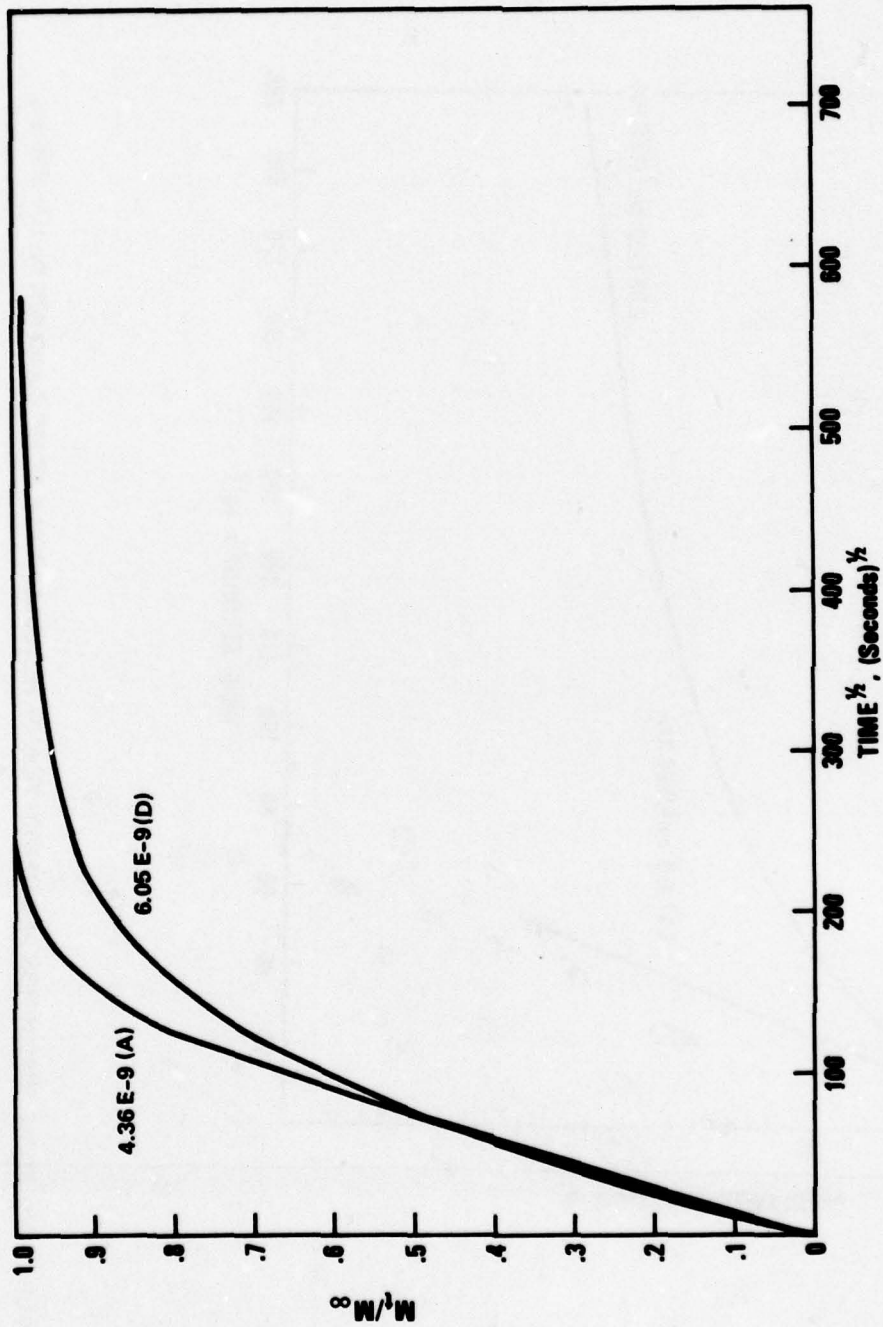
FIGURE 2 MOISTURE ABSORPTION AND DESORPTION OF HERCULES 3501-6 (L = .029 cm) AT 50° C AND 80% RH
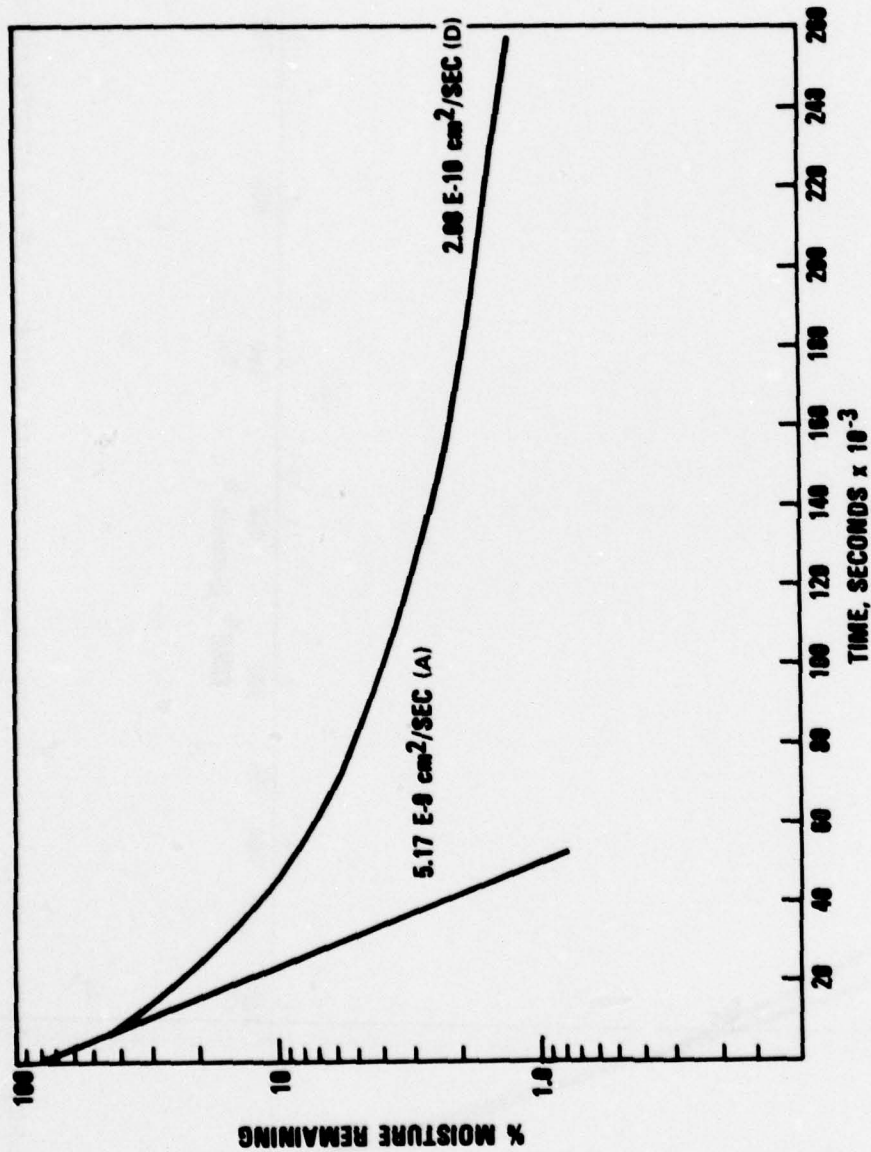
FIGURE 3 MOISTURE ABSORPTION AND DESORPTION OF HERCULES 3501-6 AT 50° C AND 80% RH (L = .024 cm).

Table 1. Diffusion Coefficients of Hercules 3501-6 Epoxy Resin (Corrected for Edge Effects)

RH (%)	Temperature (°C)	Equil. Conc. (Wt. %)	$\bar{D}_1^A$ (cm²/sec)10⁻⁹	$\bar{D}_1^D$ (cm²/sec)10⁻⁹	$D_f^A(C)$ (cm²/sec)10⁻⁹	$D_f^D(0)$ (cm²/sec)10⁻⁹	D(C)/D(0)
7	50	0.507	2.92	2.14	1.88	0.197ᵃ	10.3
15	50	1.037	3.85	2.14	3.83	0.106	21.0
30	50	1.603	3.62	2.90	4.28	-	23.5
60	50	2.847	4.58	4.20	4.96	0.215	27.3
80	50	3.765	4.36	6.05	5.17	0.208	28.4
15	30	-	0.92	-	1.69	-	36.7
29	30	-	1.18	0.98	1.92	0.046	41.7
60	30	-	1.66	-	2.01	-	43.7
80	30	-	1.54	2.71	1.80	-	39.1

[a] From these data (at 50°C) one can observe the experimental spread in long term measurements, a value of 0.181 x 10⁻⁹ cm²/sec was taken as an average.
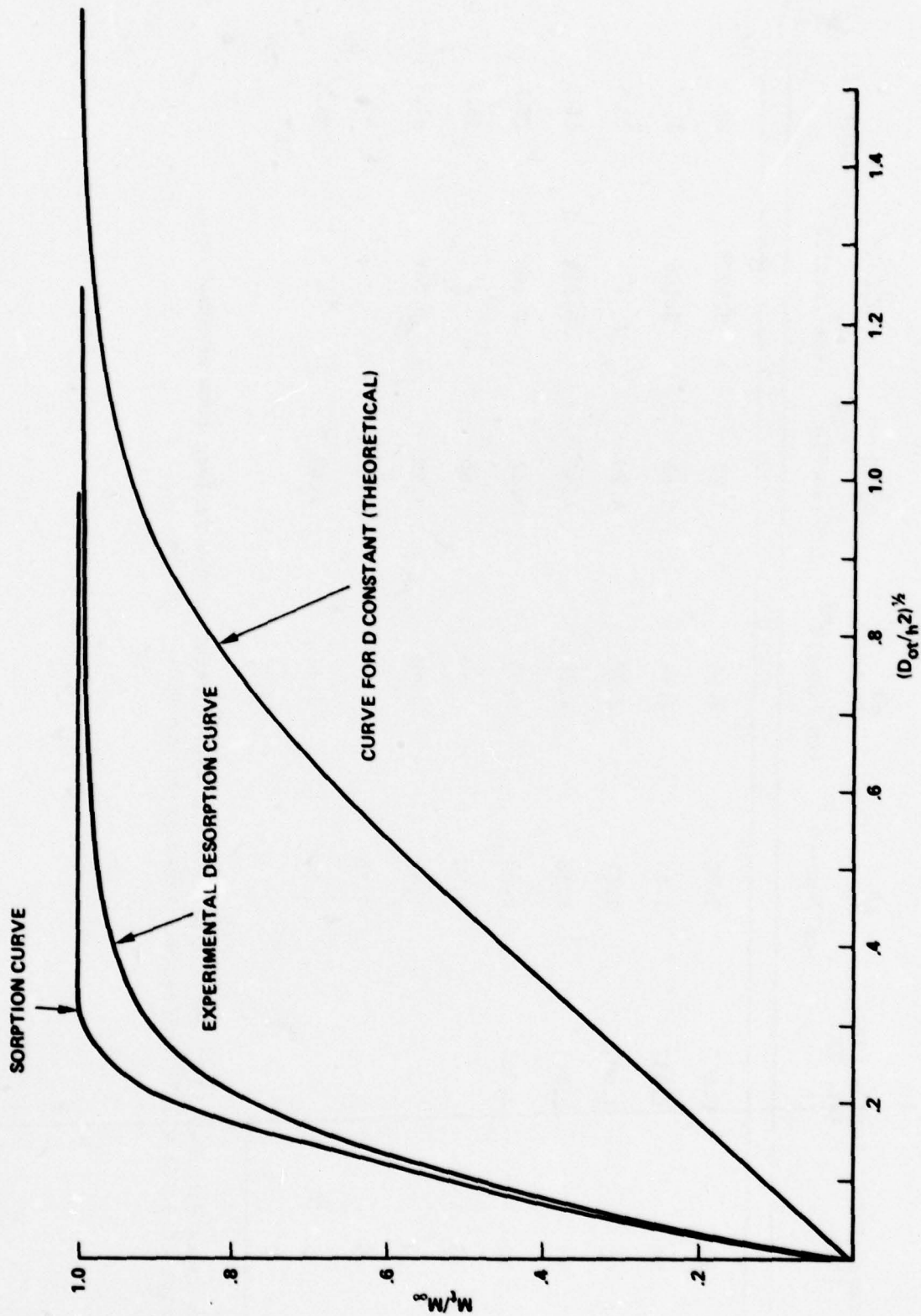
FIGURE 4 THEORETICAL AND EXPERIMENTAL SORPTION AND DESORPTION CURVES
FOR 3501-6 RESIN (D(0) = 2.08 E -10) cm^2/sec AT 50° C AND 80% R.H.
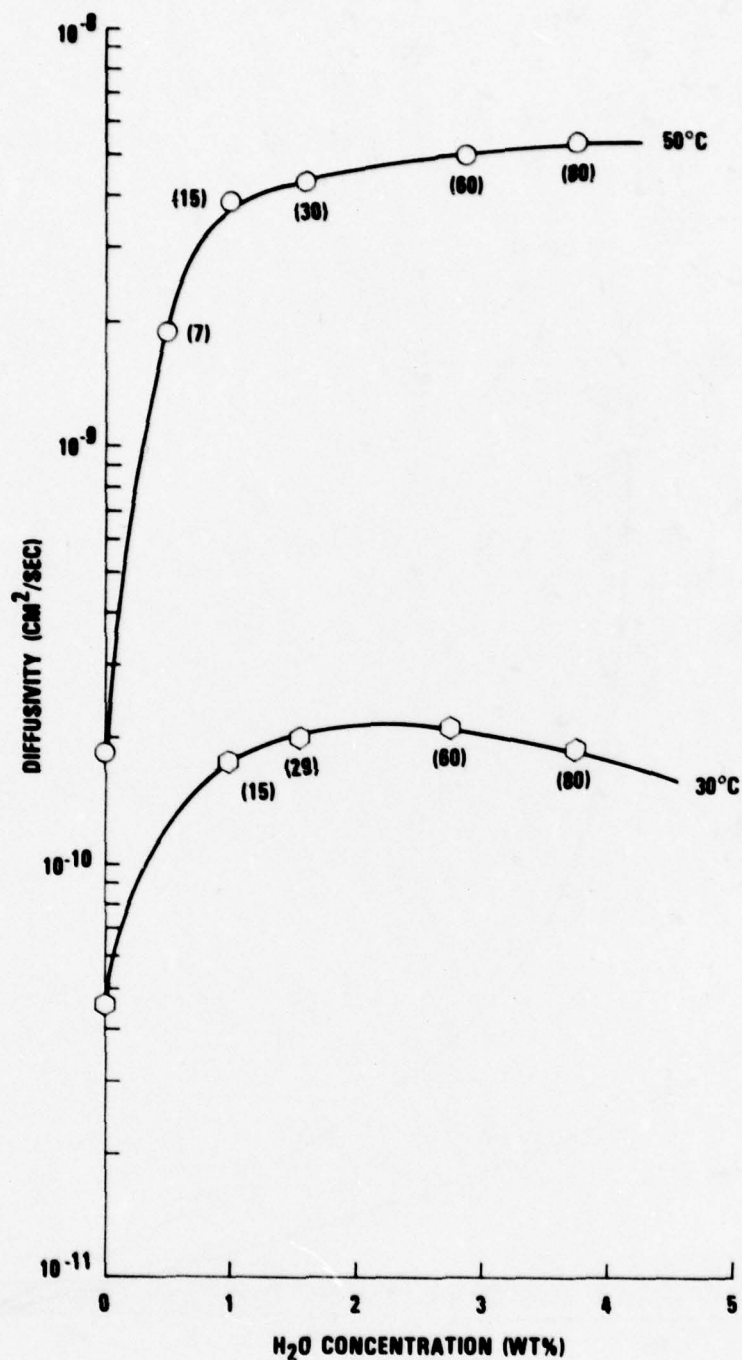
FIGURE 5   MOISTURE DIFFUSIVITY D(C) OF HERCULES 3501-6 EPOXY RESIN.
(FOR 3501-6/AS COMPOSITES (V_f = 0.65) D (C) IS MULTIPLIED BY
0.25) THE NUMBERS IN PARENTHESIS INDICATE THE REL. HUMIDITY
AT WHICH D(C) WAS MEASURED.   D(o) WAS OBTAINED FROM
DESORPTION MEASUREMENTS

FIGURE 6 CONCENTRATION OF DEPENDENCE OF THE MOISTURE DIFFUSION COEFFICIENT OF HERCULES 3501-6 EPOXY RESIN.

FIGURE 7 EQUILIBRIUM CONCENTRATION OF MOISTURE IN HERCULES 3501—6

FIGURE 8   EQUILIBRIUM SORPTION OF WATER IN HERCULES 3501-6 EPOXY RESIN

From Figure 5, it appears that the moisture diffusion coefficient goes through a maximum at least at ambient temperature. Such a behavior is not unknown and it may occur with diffusants that can readily form hydrogen bridges and therefore lead to self condensation.
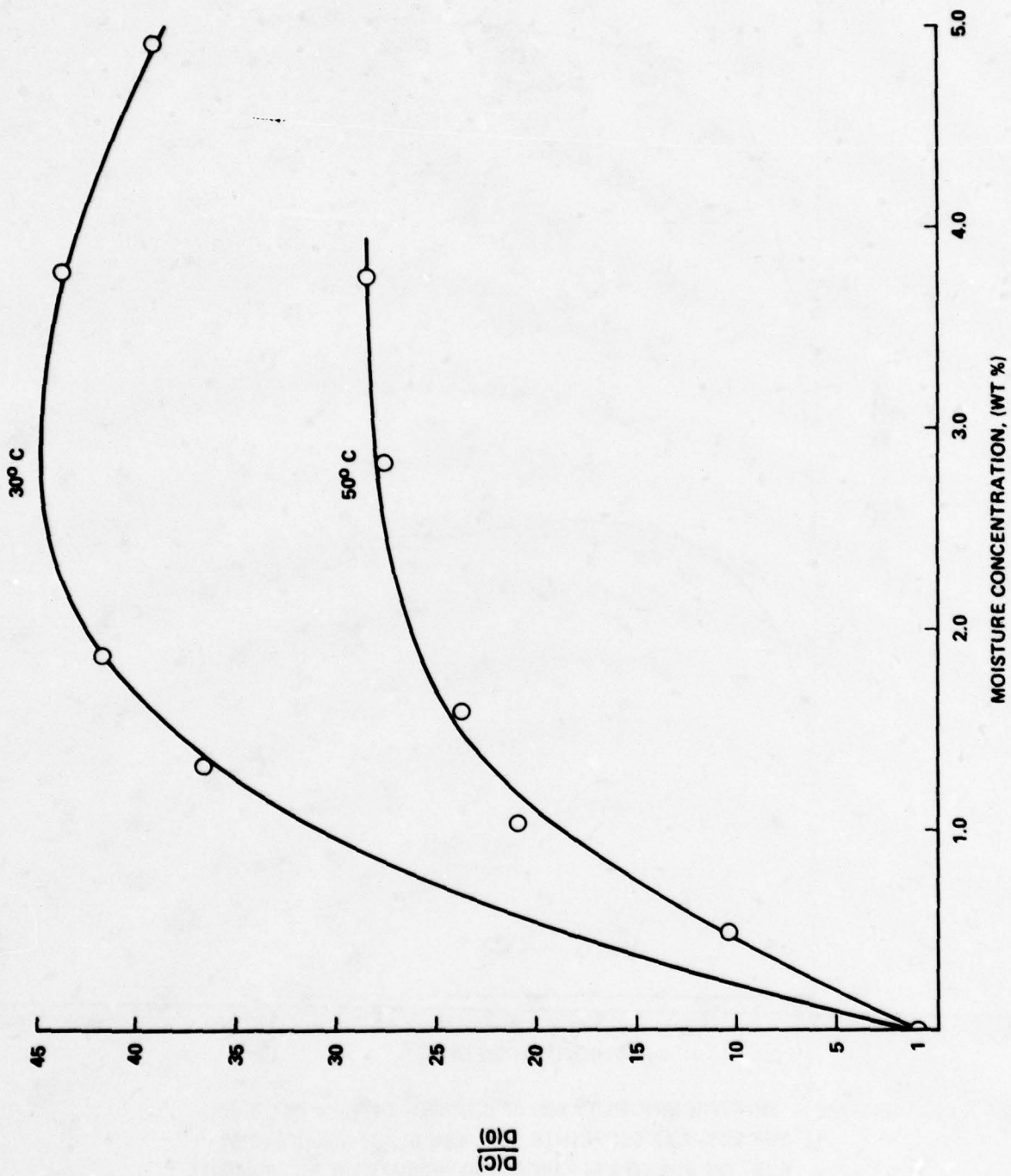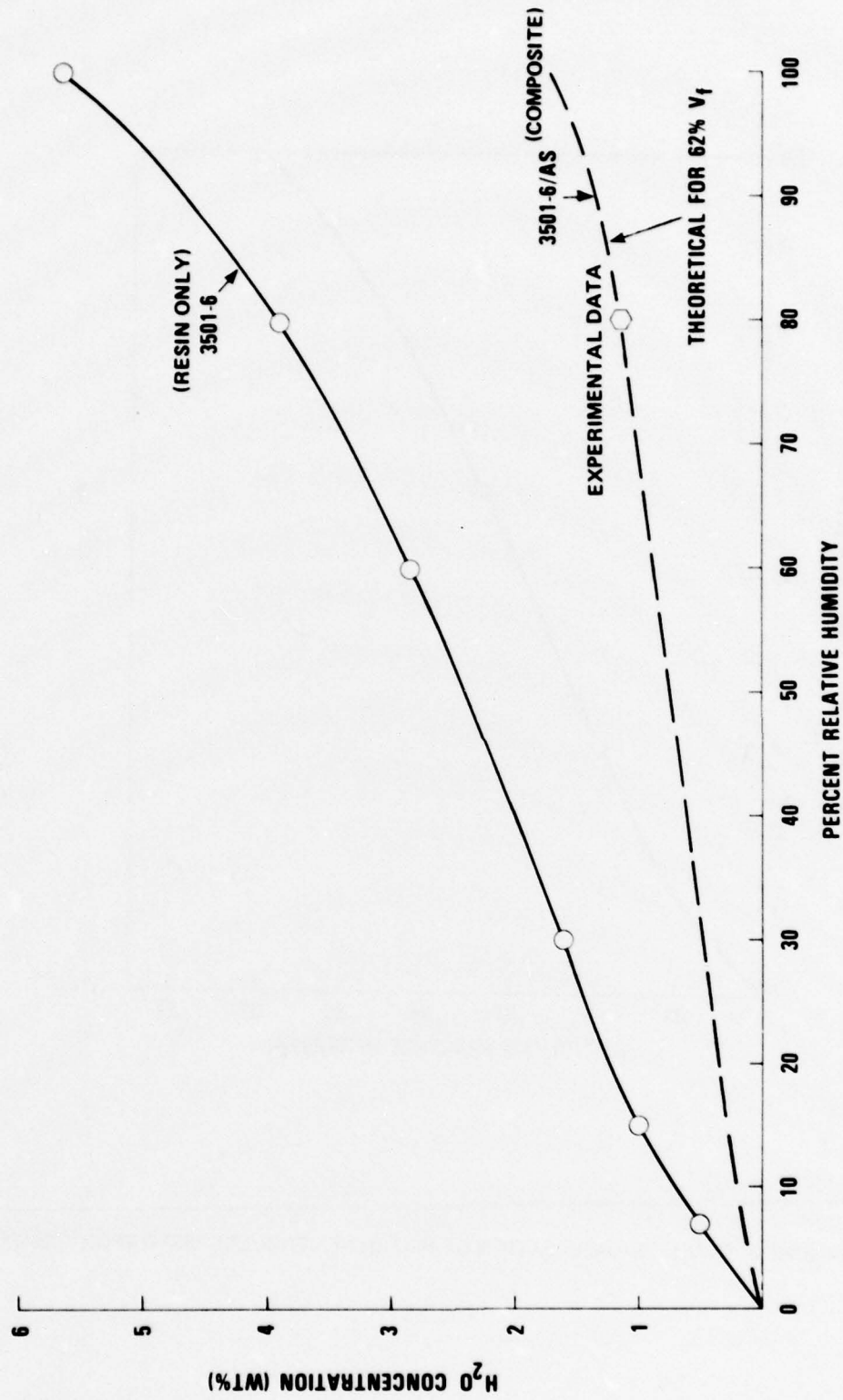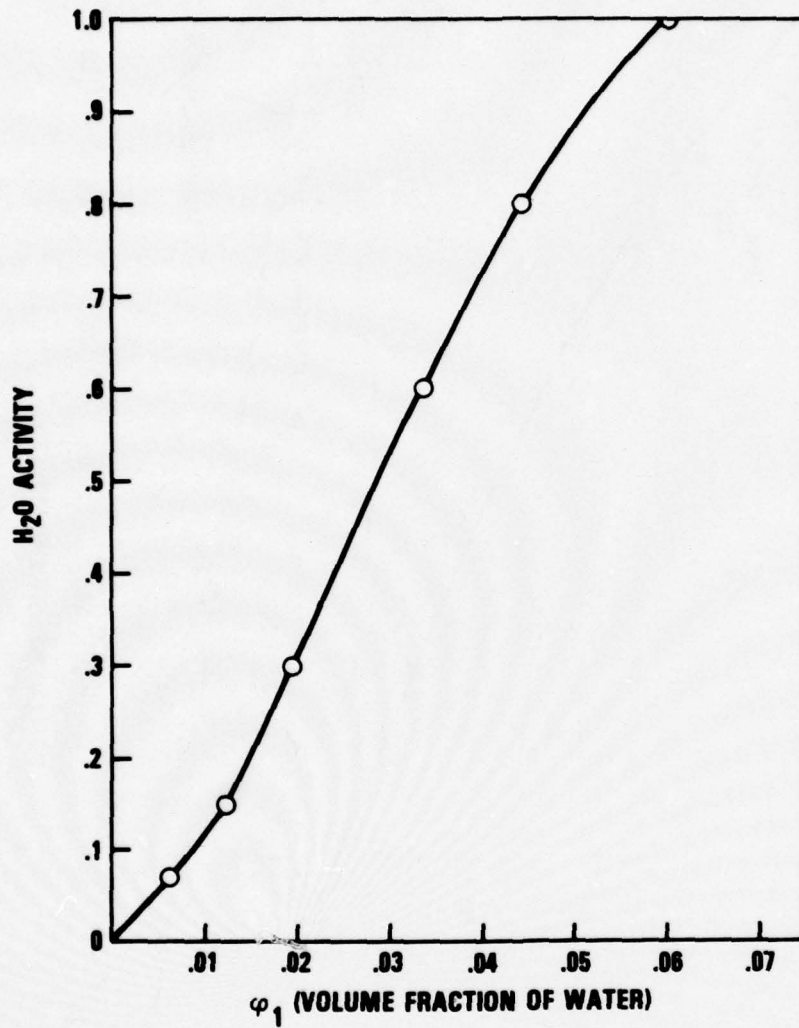
If such a self condensation (clustering) of a solvent in a polymer occurs, the diffusion of the solvent will be reduced since the size of the diffusant has increased to form a dimer or even larger condensation clusters. The answer of whether or not such a condensation occurs may be obtained from statistical thermodynamics of polymers.

Based on the investigation of McMillan and Mayer[24] on the statistical thermodynamics of multicomponent systems, Zimm has proposed two forms of "clustering functions."[25-27]

$$\frac{G_{11}}{V_1} = -\phi_2 \left[\frac{\partial (a_1/\phi_1)}{\partial a_1} \right]_{p,T} -1$$

and
$$C_1 G_{11} = \frac{\phi_1 G_{11}}{V_1} = \phi_2 \left(\frac{\partial \ln \phi_1}{\partial \ln a_1} \right)_{p,T} -1$$

This is to be understood that the mean number of type 1 molecules ($=H_2O$) in the neighborhood of a given type 1 molecule in excess of the mean concentration of type 1 molecule is $\phi_1 G_{11}/V_1 = C_1 G_{11}$, where ϕ_1, V_1 and C_1 are the volume fraction, partial molar volume and molar concentration of component 1, respectively.

This clustering function is easily derived from the sorption isotherm (Figure 8), from which $a_1 \phi_1$ vs a_1 is obtained (Figure 9 and Table 2). A graphical differentiation of the curve of Figure 9 gives finally G_{11}/V_1 or $C_1 G_{11}$. The latter function is shown in Figure 10. As a comparison, the clustering function of unstretched Nylon 66 is also shown, where the sorption data were taken from the literature.[28]

24. McMillan, W.G., and Mayer, J., _J. Chem. Phys._, _13_, 276, 1945.

25. Zimm, B.H., _J. Chem. Phys._, _14_, 164, 1945.

26. Zimm, B.H., _ibid_, _21_, 934, 1953.

27. Zimm, B.H., and Lundberg, J.L., _J. Phys. Chem._, _52_, 425, 1956.

28. Bull, H.B., _J. Amer. Chem. Soc._, _66_, 1499, 1949.
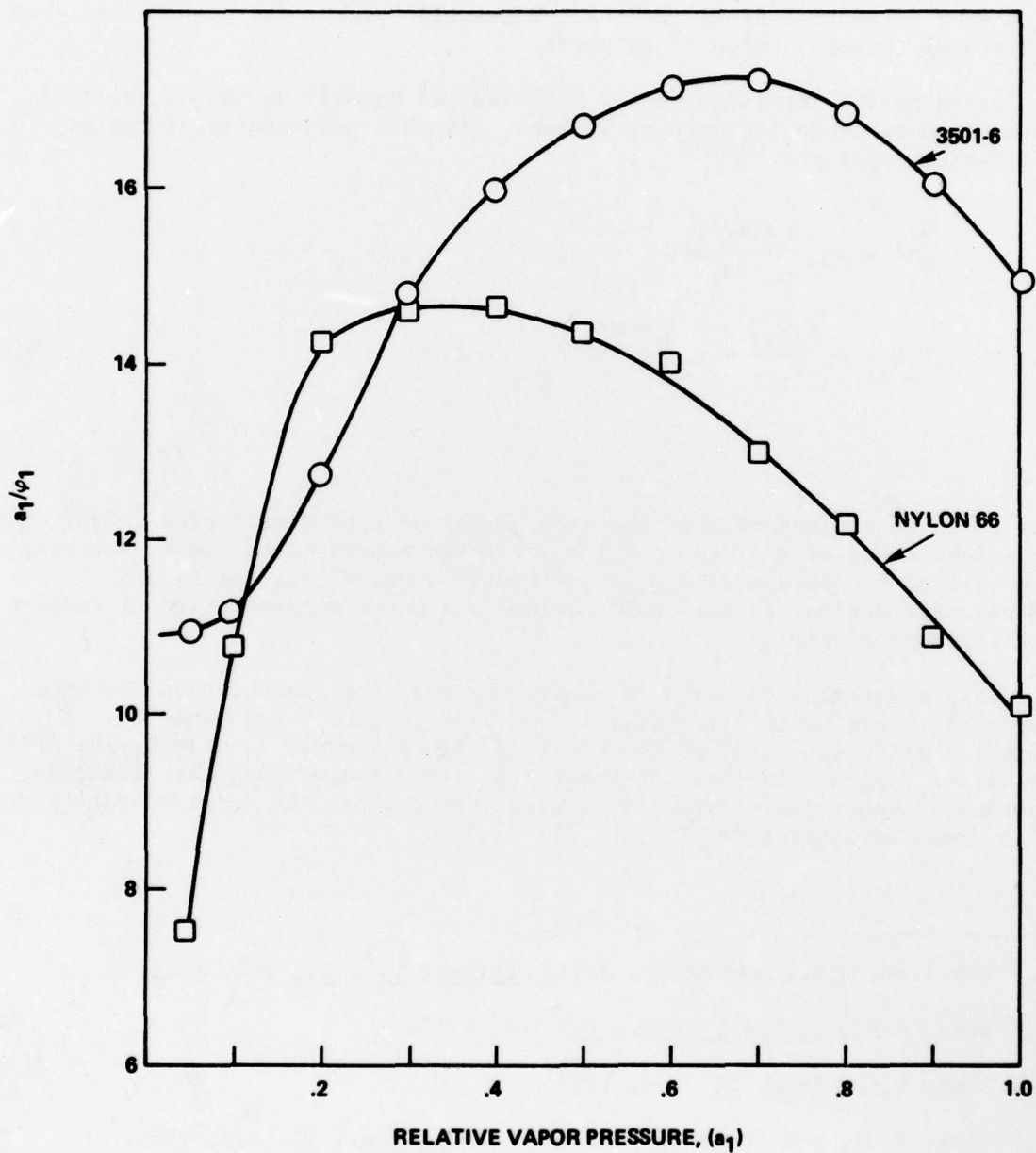
FIGURE 9 ϕ/a_1 VERSUS a_1 OF HERCULES 3501-6 EPOXY RESIN.

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Table 2. Zimm's Clustering Functions G_{11}/V_1 and C_1G_{11} of Hercules 3501-6 Epoxy Resin

H_2O Activity a_1	H_2O Weight %	H_2O Volume Fractional ϕ_1	a_1 / ϕ_1	Polymer Volume Fraction ϕ_2	$\dfrac{\Delta(a_1/\phi_1)}{\Delta a_1}$	$\dfrac{G_{11}}{V_1}$	C_1G_{11}
.05	.36	.0046	10.93	.9954	-	-	-
.1	.71	.0090	11.13	.9910	7.0	-7.93	-.0713
.2	1.25	.0157	12.73	.9843	18.0	-18.7	-.2935
.3	1.62	.0203	14.80	.9797	16.6	-17.3	-.351
.4	2.01	.0250	15.98	.9750	10.	-10.75	-.269
.5	2.42	.0300	16.68	.9700	5.8	-6.6	-.198
.6	2.84	.0350	17.14	.9650	3.00	-3.89	-.136
.7	3.32	.0407	17.21	.9593	-1.02	-0.02	-.0008
.8	3.90	.0474	16.86	.9526	-5.89	4.61	.218
.9	4.65	.0560	16.06	.9452	-9.10	7.60	.426
1.0	5.63	.0673	14.91	.9327	-11.6	9.81	.660
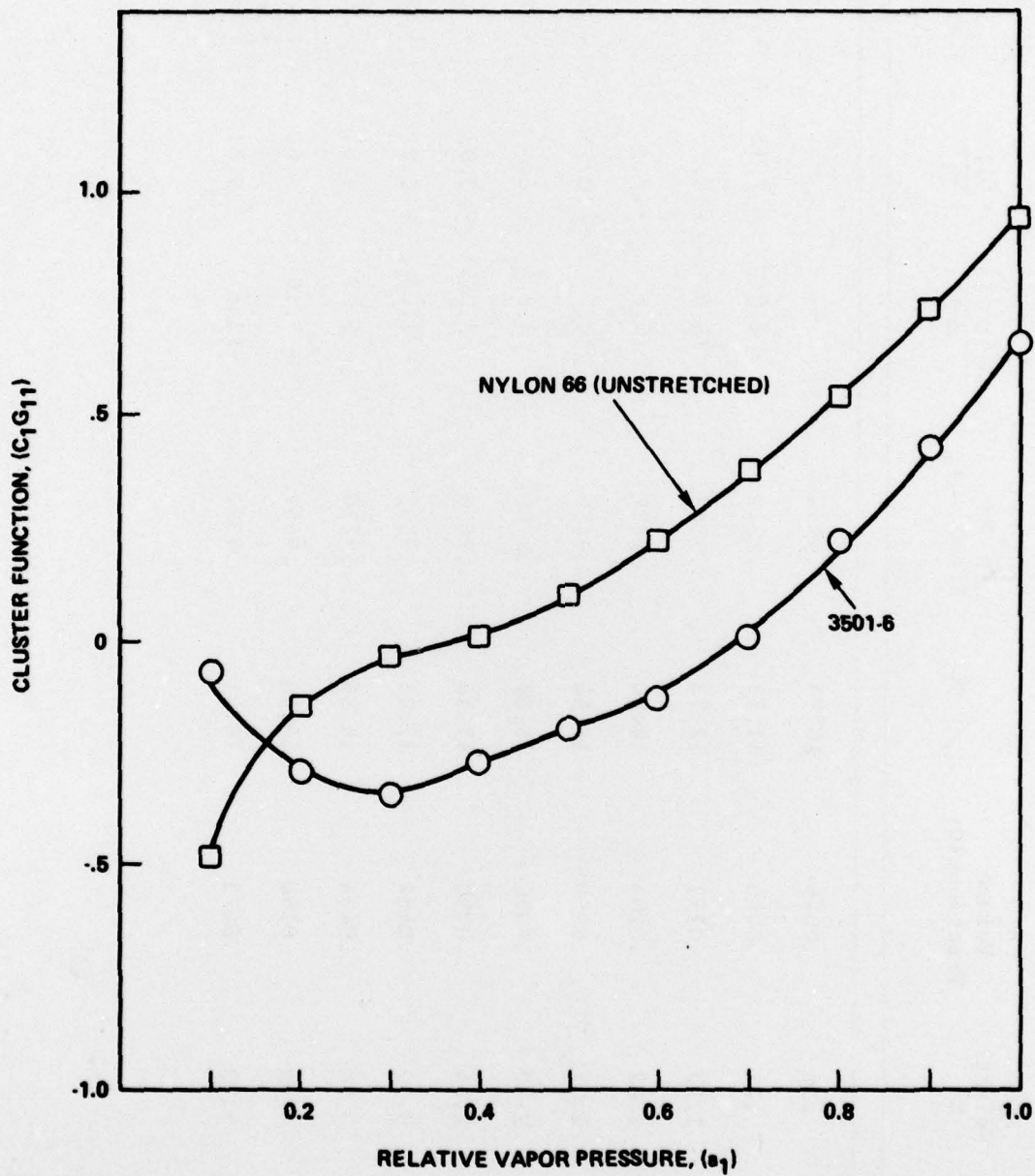
FIGURE 10 ZIMM'S CLUSTER FUNCTION (C_1G_{11}) OF HERCULES 3501-6 EPOXY RESIN AS A FUNCTION OF THE RELATIVE MOISTURE EQUILIBRIUM VAPOR PRESSURE.

Since C_1G_{11} is the mean number of water molecules near a given water molecule in excess of the mean concentration, the mean size of the cluster is $C_1G_{11}+1$, which indicates that the size of the cluster increases rapidly at higher relative humidity equilibrium concentrations.

Similar results have been reported in the literature by Starkweather[29] for cellulose, keratin, collagen, serum albumin, polyvinyl acetate and polymethyl methacrylate.

29. Starkweather, H.W., <u>Polymer Letters</u>, <u>1</u>, 133, 1963.

CONCLUSIONS AND RECOMMENDATIONS

1. The moisture diffusion coefficient of Hercules 3501-6 has been determined at 30` and 50`C as a function of concentration.

2. It was found that, at very low moisture concentration, the diffusion coefficient is low, while at concentrations between 1 and 5% of moisture (equivalent to 30-90% relative humidity equilibrium concentration), the diffusion coefficient is rather flat and seems to have a maximum at lower temperatures (30`C). This behavior can be rationalized from a clustering mechanism of water at higher moisture concentrations. Such clustering reduces the diffusant mobility and thus its diffusion coefficient.

3. The concentration dependence was directly determined from the long term sorption experiments according to Frensdorff's method.

4. It is recommended that diffusion studies also be made on stressed resin and composite samples in order to obtain information on whether or not these materials show stress induced diffusion.

ACKNOWLEDGEMENT

APPENDIX A

Sample Preparation

The resin Hercules 3501-6 was obtained from the manufacturer (Hercules Bacchus, Utah) and kept stored in a freezer.

The resin was heated to 93°C at which temperature it was degassed under vacuum. Then the liquid resin was cast into a plate mold and cured under the following conditions: the resin was kept for 1 hour each at the following temperatures: 100°, 115°, 124°, 130°, and 150°C. The final cure was then 10 hours at 177°C. The resin was then allowed to cool and was machined into thin (0.024 cm) plate samples.

Sorption Chamber and Sorption Measurements

Figure 1 shows a schematic of the sorption apparatus which consists of a Cahn electrobalance, a weighing chamber, a vapor generator, a capacitance manometer with a range from 0.1 to 1,000 mm of Hg pressure, a constant temperature bath, a 5 buffer vapor reservoir, a vacuum pump, and a recorder with a sensitivity of 0.002 mg. The temperature in the wooden isolated chamber was usually held at 3°C higher than in the sample chamber by air circulation with two blowers. The sample chamber was held at constant temperature by circulating water through a heating jacket.

The predried sample was transferred into the weighing chamber and vacuum was applied with the valves V_1, V_2, and V_3 open. The water temperature of the constant temperature bath was raised to 80°C to remove moisture that may have been sorbed during the sample transfer. Then the temperature was lowered to the desired measurement temperature. Valve V_2 was closed and valve V_4 was opened till the desired vapor pressure was reached (as indicated by the pressure gauge). Instead of adjusting the vapor pressure directly from a reservoir of liquid water, it is also possible to keep a binary salt water mixture in the vapor generator which restricts the relative pressure to only certain fixed values (dependent on the kind of salt used and on the measurement temperature). The sorption was run till equilibrium was attained.

At relative humidities higher than 80% the Cahn balance became unstable. Whenever possible it is desirable to do the entire series of sorption and desorption measurements without removal of the sample. It took about 100 seconds till the pressure was reached at which the measurement was to be

carried out, especially at the high relative vapor pressures. (If by acci-
dent the desired measurement pressure is exceeded, this can be easily recti-
fied by opening valve V_2 to the vacuum pump.) It is also desirable to be
able to control the valves from outside the insulation box.

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